Interaction of Triplet Excited States of Ketones with Nucleophilic Groups: (π,π*) and (n,π*) vs. (σ*,π*) States. Substituent-Induced State Switching in Triplet Ketones

Götz Bucher[a]*

[a]WestCHEM, School of Chemistry, University of Glasgow, University Avenue, Glasgow G12 8QQ, United Kingdom. E-mail: goebu@chem.gla.ac.uk

Abstract

Intramolecular interaction of ketone triplet excited states with nucleophilic substituents is investigated by studying the electronic properties of phenalenone and a range of phenalenones functionalized in position 9 as a model system. In accordance with literature, a (π,π*) triplet excited state is predicted for phenalenone. Similarly, 9-fluoro-, 9-chloro- and 9-methoxyphenalenone are calculated to have (π,π*) lowest triplet excited states, whereas the lowest triplet states of 9-bromo-, 9-iodo, 9-methylthio, and 9-dimethylaminophenalenone are predicted to have (σ*,π*) character. As a result of the interaction between halogen and oxygen lone pairs increasing with increasing orbital size, the antibonding linear combination of substituent lone pairs with oxygen lone pairs sufficiently rises in energy to change the character of the lowest triplet excited state of the 9-substituted phenalenones from (π,π*) to (σ*,π*). These unusual triplet excited states or exciplexes should essentially behave like (n,π*) triplets states, but will differ from pure (n,π*) states by showing significant spin densities at the substituent heteroatoms, predicted to reach values of 0.25 for 9-iodophenalenone, and ca. 0.5 for 9-dimethylaminophenalenone. Vertical T_1-T_2 excitation energies calculated indicate that the stabilization of the (σ*,π*) relative to the (π,π*) state can reach 1 eV. Preliminary calculations on the triplet excited states of 2-iodobenzophenone, 4-iodo-2-butanone, and iodoacetone indicate that intramolecular triplet exciplex formation should be a general phenomenon, as long as the ring being formed is at least a five-membered ring.

Introduction

Triplet excited states come in a variety of types, each showing a different reactivity. Annelated benzenoid π-systems like naphthalene and anthracene or electron-rich ketones have triplet excited states, in which an electron from a bonding π-type orbital has been promoted to an antibonding π*-type orbital. Such (π,π*)-triplet excited states typically do not show a pronounced free-radical type reactivity, but upon reaction with triplet molecular oxygen do form singlet oxygen efficiently.[1] If typical ketones such as benzophenone or acetone are excited, on the other hand, the lowest triplet excited state formed with high quantum yield is of (n,π*) type. Here, an electron is excited from a non-bonding orbital at the carbonyl oxygen atom (a lone pair), to a π* orbital. This type of electronic excitation creates significant spin density at the carbonyl oxygen atom, which consequently behaves like a highly-reactive oxygen-centered radical, and is efficiently quenched by hydrogen-donor molecules like benzhydrol, 1,4-cyclohexadiene, or tributylstannane.[2,3] If no sufficiently low-lying empty π*-orbitals are available to accept an electron, electrons can also be promoted to antibonding σ*-type orbitals. Thus, (π,σ*) excited states are observed in the case of certain heteroaromatic compounds.[4] Two adjacent atoms carrying lone pairs, such as found in disulfides, peroxides,

diselenides, or simple dihalogen molecules, have a doubly-occupied π*-type orbital. The lowest triplet excited state of such compounds is of (π*,σ*) type, as was found experimentally[5] and later computationally[6] for lipoic acid. The lowest triplet excited state of hydrogen peroxide, molecular chlorine[7] or fluorine, analogously are calculated to be of (π*,σ*) type.[8] Hydrazine, finally, has a high-energy Rydberg-type triplet excited state, where an electron is promoted from the doubly-occupied antibonding π* orbital of the N-N bond to higher (2s, 3s, 4s) s-type atomic orbitals of the four hydrogen atoms.[8]

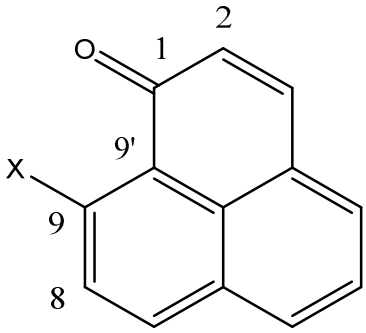
Quenching of triplet excited states can occur via a variety of mechanisms. Apart from triplet energy transfer to typical triplet quenchers like 1,3-dienes or molecular oxygen, quenching reactions may involve hydrogen abstraction, or reaction with nucleophiles. The latter reaction has been known to result in the formation of exciplexes,[9-11] which may be associated with full or partial electron transfer,[11] and it may be followed by subsequent hydrogen atom or proton transfer.[9]

Phenalenone **1** is an aromatic ketone that for a long time has served as a workhorse compound in studies on ketone photophysics and on singlet oxygen chemistry. Its lowest triplet excited state is of (π,π*) type, and it reacts efficiently with triplet molecular oxygen, yielding singlet oxygen O_2 ($^1\Delta_g$) in a quantum yield of Φ = 1.0.[12,13] If it is phenyl-substituted in 9-position, photochemical addition of the carbonyl oxygen atom on the *ortho*-position of the 9-phenyl substituent occurs, resulting in the formation of a strongly reducing quinoid intermediate that is oxidised to a phenalenyl-type cation or radical with great ease.[14-17] Aiming at a more variable and convenient access to 9-substituted phenalenones, we recently prepared 9-trifluoromethanesulfonyloxy- and 9-iodophenalenone.[18] I now report on quantum chemical calculations on the lowest triplet excited state of 9-iodophenalenone, as well as of a series of other 9-substituted phenalenones, in a study aimed at elucidating the intramolecular interaction of ketone triplet excited states with nucleophiles.

Computational methods: calculations were performed employing the Gaussian09[19] suite of programs. Geometry optimizations were done using the M05-2X[20] and M06[21] functionals. The influence of solvation by a polar-aprotic solvent (DMF) was accounted for using a polarizable continuum model (scrf=pcm).[22,23] All stationary points optimized were fully characterized via a vibrational analysis. As basis set, the Stuttgart-Dresden (SDD) basis set was used throughout.[24,25] In addition, a number of calculations were performed using Dunning's cc-pVTZ[26-28] basis set.

Results and Discussion

The singlet ground states of phenalenone **1** and the 9-substituted phenalenones were optimized at the M05-2X/SDD, M06/SDD, M06/SDD(pcm,DMF) and M06/cc-pVTZ (except X = I) levels of theory. Table 1 lists relevant geometric parameters of optimized ground-state and lowest triplet excited state structures of **1**-**8.**



Scheme 1: Numbering of atoms in phenalenones

Table 1: Selected geometric parameters of ground-states (normal font) and lowest triplet states (*in italics*) of phenalenone and 9-substituted phenalenones

	X	Method	R(O-X), S_0 *R(O-X), T_1*	A(C9'-C1-O), S_0 *A(C9'-C1-O), T_1*	A(C9'-C9-X), S_0 *A(C9'-C9-X), T_1*	R(C1-O), S_0 *R(C1-O), T_1*	R(C_9-X), S_0 *R(C_9-X), T_1*
1	H	M05-2X/ SDD	2.502 *2.503*	121.9 *120.4*	118.3 *118.3*	1.256 *1.329*	1.083 *1.081*
1	H	M06/SDD	2.505 *2.503*	122.1 *120.8*	118.0 *118.0*	1.258 *1.307*	1.087 *1.085*
1	H	M06/SDD (pcm, DMF)	2.526 *2.529*	122.0 *121.0*	118.6 *118.5*	1.268 *1.305*	1.086 *1.085*
1	H	M06/ cc-pVTZ	2.485 *2.483*	122.2 *121.3*	118.0 *117.9*	1.216 *1.246*	1.083 *1.081*
2	F	M05-2X/ SDD	2.705 *2.702*	123.5 *122.6*	121.3 *120.2*	1.253 *1.336*	1.378 *1.384*
2	F	M06/SDD	2.710 *2.709*	123.5 *122.9*	121.3 *120.3*	1.254 *1.307*	1.370 *1.376*
2	F	M06/SDD (pcm, DMF)	2.710 *2.717*	123.4 *123.0*	120.8 *120.0*	1.265 *1.305*	1.380 *1.388*
2	F	M06/ cc-pVTZ	2.669 *2.666*	123.4 *123.1*	121.2 *120.1*	1.214 *1.244*	1.315 *1.320*
3	Cl	M05-2X/ SDD	2.881 *2.903*	123.6 *123.0*	124.0 *123.4*	1.253 *1.332*	1.794 *1.800*
3	Cl	M06/SDD	2.889 *2.909*	123.7 *123.4*	123.6 *123.2*	1.254 *1.306*	1.795 *1.800*
3	Cl	M06/SDD (pcm, DMF)	2.904 *2.927*	123.6 *123.5*	123.5 *123.1*	1.264 *1.303*	1.806 *1.813*
3	Cl	M06/ cc-pVTZ	2.840 *2.863*	123.6 *123.5*	123.6 *123.2*	1.214 *1.244*	1.728 *1.732*
4	Br	M05-2X/	2.941	123.4	124.7	1.253	1.932

		SDD	*2.730*	*122.1*	*120.0*	*1.377*	*1.936*
4	Br	M06/SDD	2.949 *2.665*	123.5 *121.7*	124.5 *118.9*	1.255 *1.360*	1.930 *1.939*
4	Br	M06/SDD (pcm, DMF)	2.980 *3.001*	123.5 *123.4*	124.7 *124.3*	1.265 *1.303*	1.940 *1.947*
4	Br	M06/ cc-pVTZ	2.915 *2.611*	123.4 *121.8*	124.6 *118.7*	1.214 *1.307*	1.887 *1.887*
5	I	M05-2X/ SDD	3.031 *2.680*	123.1 *121.9*	125.8 *118.5*	1.254 *1.371*	2.127 *2.121*
5	I	M06/SDD	3.029 *2.677*	123.2 *121.9*	125.5 *118.3*	1.256 *1.357*	2.127 *2.124*
5	I	M06/SDD (pcm, DMF)	3.055 *2.657*	123.0 *121.7*	125.7 *118.1*	1.265 *1.360*	2.135 *2.124*
6	MeO	M05-2X/ SDD	2.658 *2.666*	124.8 *123.9*	118.6 *117.1*	1.256 *1.339*	1.368 *1.374*
6	MeO	M06/SDD	2.651 *2.662*	124.7 *124.0*	118.1 *116.7*	1.257 *1.309*	1.362 *1.368*
6	MeO	M06/SDD (pcm, DMF)	2.682 *2.691*	124.7 *124.2*	118.5 *117.4*	1.270 *1.306*	1.362 *1.374*
6	MeO	M06/ cc-pVTZ	2.616 *2.620*	124.2 *123.8*	118.3 *116.9*	1.217 *1.245*	1.330 *1.335*
7	MeS	M05-2X/ SDD	2.678 *2.388*	121.9 *119.8*	121.1 *116.5*	1.261 *1.355*	1.810 *1.817*
7	MeS	M06/SDD	2.668 *2.501*	122.0 *120.7*	120.6 *118.0*	1.264 *1.349*	1.813 *1.822*
7	MeS	M06/SDD (pcm, DMF)	2.708 *2.488*	122.1 *120.5*	121.0 *117.8*	1.273 *1.351*	1.815 *1.822*
7	MeS	M06/ cc-pVTZ	2.619 *2.392*	121.9 *120.3*	120.4 *117.1*	1.224 *1.295*	1.756 *1.759*
8	Me_2N	M05-2X/ SDD	2.897 *2.170*	123.9 *117.8*	123.9 *114.5*	1.268 *1.345*	1.369 *1.439*
8	Me_2N	M06/SDD	2.919 *2.276*	124.0 *118.9*	123.9 *116.1*	1.268 *1.337*	1.374 *1.433*
8	Me_2N	M06/SDD (pcm, DMF)	2.945 *2.310*	124.0 *119.0*	123.7 *116.9*	1.279 *1.331*	1.368 *1.434*
8	Me_2N	M06/ cc-pVTZ	2.861 *2.267*	123.8 *119.3*	123.6 *116.1*	1.225 *1.288*	1.360 *1.417*

9-Halophenalenones (X = F, Cl, Br, I): In case of the singlet ground-state 9-halogen-substituted derivatives, repulsion between the halogen and the carbonyl group invariably resulted in an increase of the X-O distance via widening of the OCC and XCC angles, relative to parent phenalenone **1**. In the lowest triplet excited state, the phenalenones investigated show two different types of behaviour. In case of 9-fluorophenalenone **2**, and 9-chlorophenalenone **3**, the oxygen – X distances remain essentially unchanged upon triplet excitation, whereas all other derivatives calculated show a significant shortening of the oxygen – X distance in the triplet excited state. 9-Bromophenalenone **4** is calculated to be a special case in that upon triplet excitation, the O-Br distance is predicted to be shortened in the gas phase, but not in DMF solution. Figure 1 shows the optimized geometries of the

singlet ground states and lowest triplet excited states of both 9-chloro- and 9-bromophenalenone **3** and **4**.

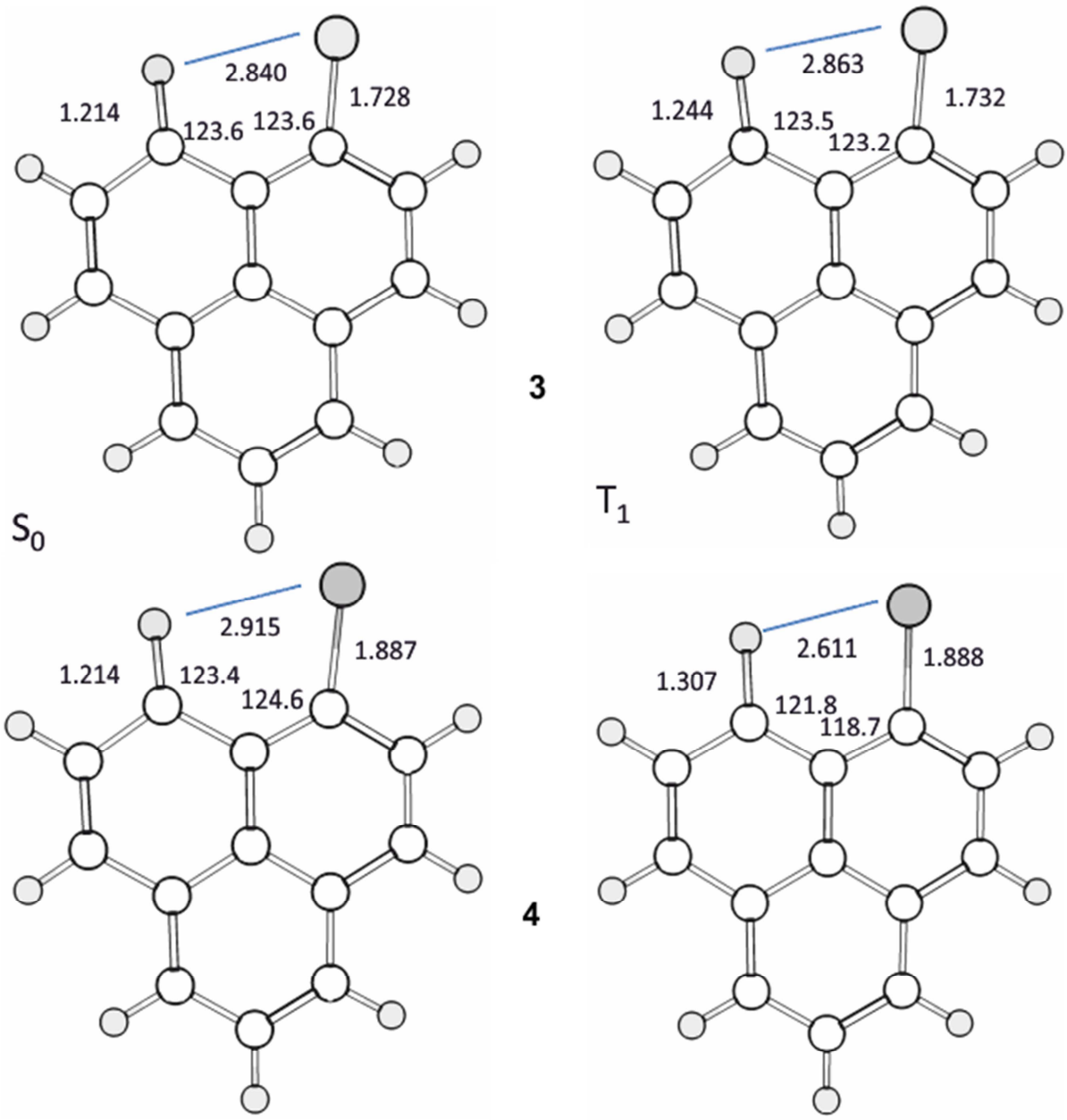


Figure 1: Optimized geometries (M06/cc-pVTZ, gas phase) of 9-chlorophenalenone **3** (top) and 9-bromophenalenone **4** (bottom). Left: singlet ground state. Right: lowest triplet excited state.

The fact that in **2** or **3**, as well as in **4** (DMF solution), the O-halogen distance remains essentially unchanged or increases marginally upon triplet excitation, whereas it is reduced in **4** (gas phase) and **5**, indicates that the nature of the triplet excited state must have changed. This is confirmed by performing a population analysis. Figure 2 shows the singly-occupied orbitals for both **3** and **4**.

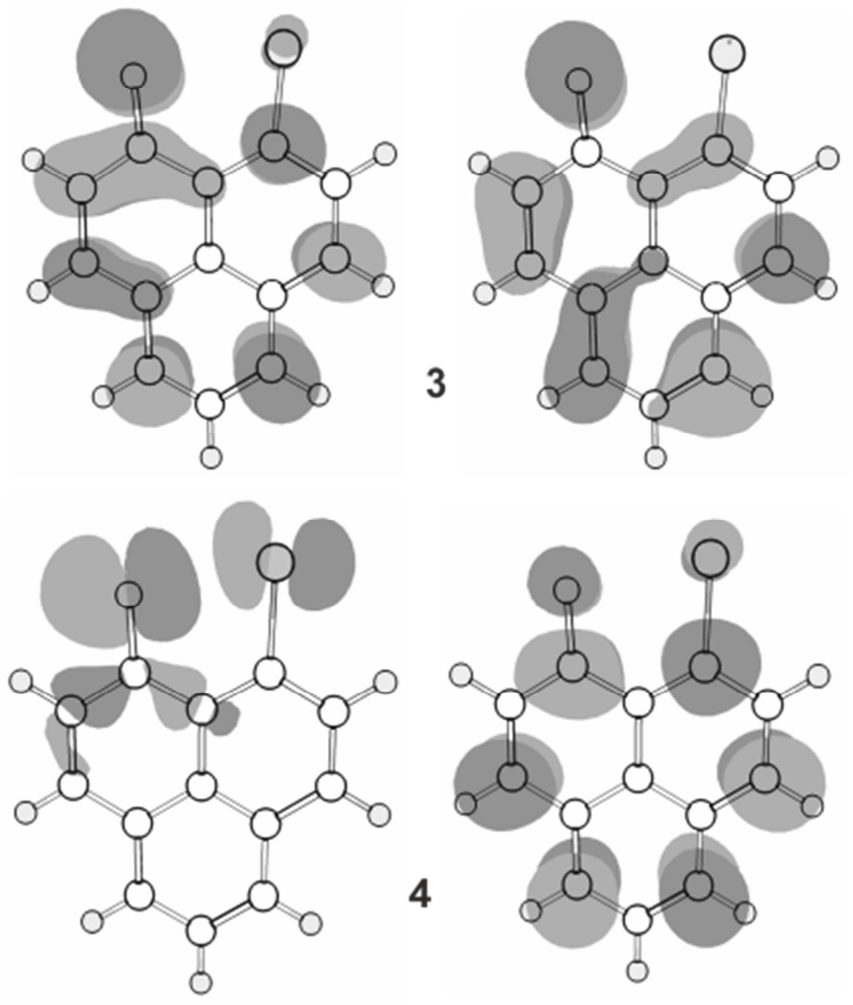


Figure 2: singly-occupied natural molecular orbitals (M05-2X/SDD, gas phase) for triplet 9-chlorophenalenone **3** (top) and triplet 9-bromophenalenone **4** (bottom). Left: HOMO-1. Right: HOMO.

Figure 2 shows that both singly occupied molecular orbitals are π-orbitals for **3**, thus demonstrating that the lowest triplet excited state of **3** is a (π,π*) state, whereas in the case of **4**, the lower singly-occupied MO is an oxygen-bromine σ* type orbital (Figure 2, bottom left). Hence, the nature of the triplet excited state switches from (π,π*) in **3** to (σ*,π*) in **4**. Destabilizing interaction of the carbonyl oxygen lone pair with a lone pair on bromine increases the energy of this antibonding linear combination to a degree that (σ*→π*) excitation becomes preferable over (π→π*) excitation as in **3**, where the energy of the chlorine lone pairs is too low to result in significant interaction with the carbonyl lone pairs.

9-Methylchalcogeno-phenalenones (X = MeO, MeS): Again, two different types of triplet states are observed. 9-Methoxyphenalenone **6** has a (π,π*) lowest triplet excited state, whereas the thiomethoxy derivative **7** has a (σ*,π*) lowest triplet state, which is again due to interaction of sulfur and carbonyl oxygen lone pairs. In this compound, however, some binding interaction between carbonyl oxygen and sulfur already appears to be present in the singlet ground state ketone. The sulfur-oxygen distance in **7** is significantly shorter than the sum of the van-der-Waals radii of sulfur

and oxygen. In fact, the oxygen-sulfur distance in **7** is calculated to be essentially equal to the oxygen-oxygen distance in 9-methoxyphenalenone **6** (**7**: M06/cc-pVTZ: R_{SO} = 2.619 Å, **6**: M06/cc-pVTZ: R_{OO} = 2.616 Å). This type of bonding situation, a three-center-four-electron interaction involving the chalcogen-methyl and chalcogen-oxygen bonds is well known in heavy-chalcogen chemistry.[29-31] The optimized singlet ground-state structure is consistent with this picture, with the O-S-C(H_3) angle very close to 180° (M06/cc-pVTZ: **7**: O-S-C(H_3) = 179.7°), whereas the corresponding angle in **6** is calculated as O-O-C(H_3) = 150.8°, at the same level of theory.

In the lowest triplet excited state of **7**, the sulfur-methyl bond is calculated to be orthogonal to the plane of the phenalenone system. This maximises interaction between the lone pairs on the carbonyl oxygen and the chalcogen atom, as required by the ($\sigma*$,$\pi*$) nature of the triplet states. Figure 3 shows optimized geometries (M06/cc-pVTZ) of both singlet ground states and lowest triplet excited states of **6** and **7**, Figure 4 the singly-occupied orbitals of the triplet states of the same molecules.

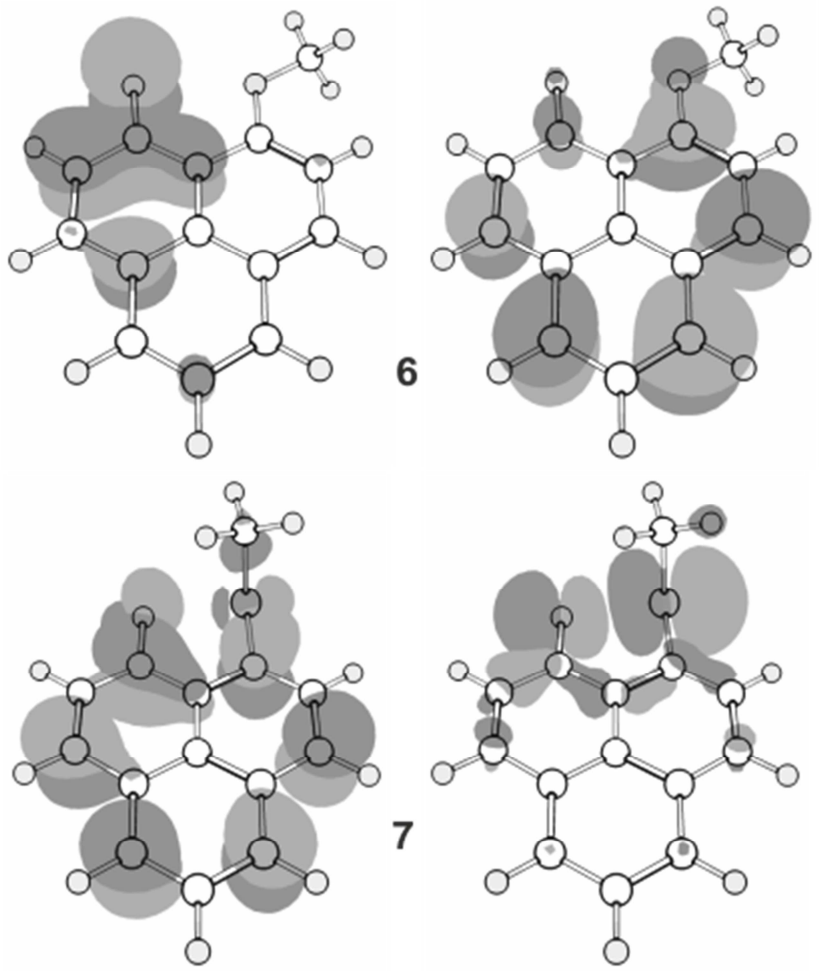


Figure 3: singly-occupied natural molecular orbitals (M05-2X/SDD, gas phase) for triplet 9-methoxyphenalenone **6** (top) and triplet 9-methylthiophenalenone **7** (bottom). Left: HOMO-1. Right: HOMO.

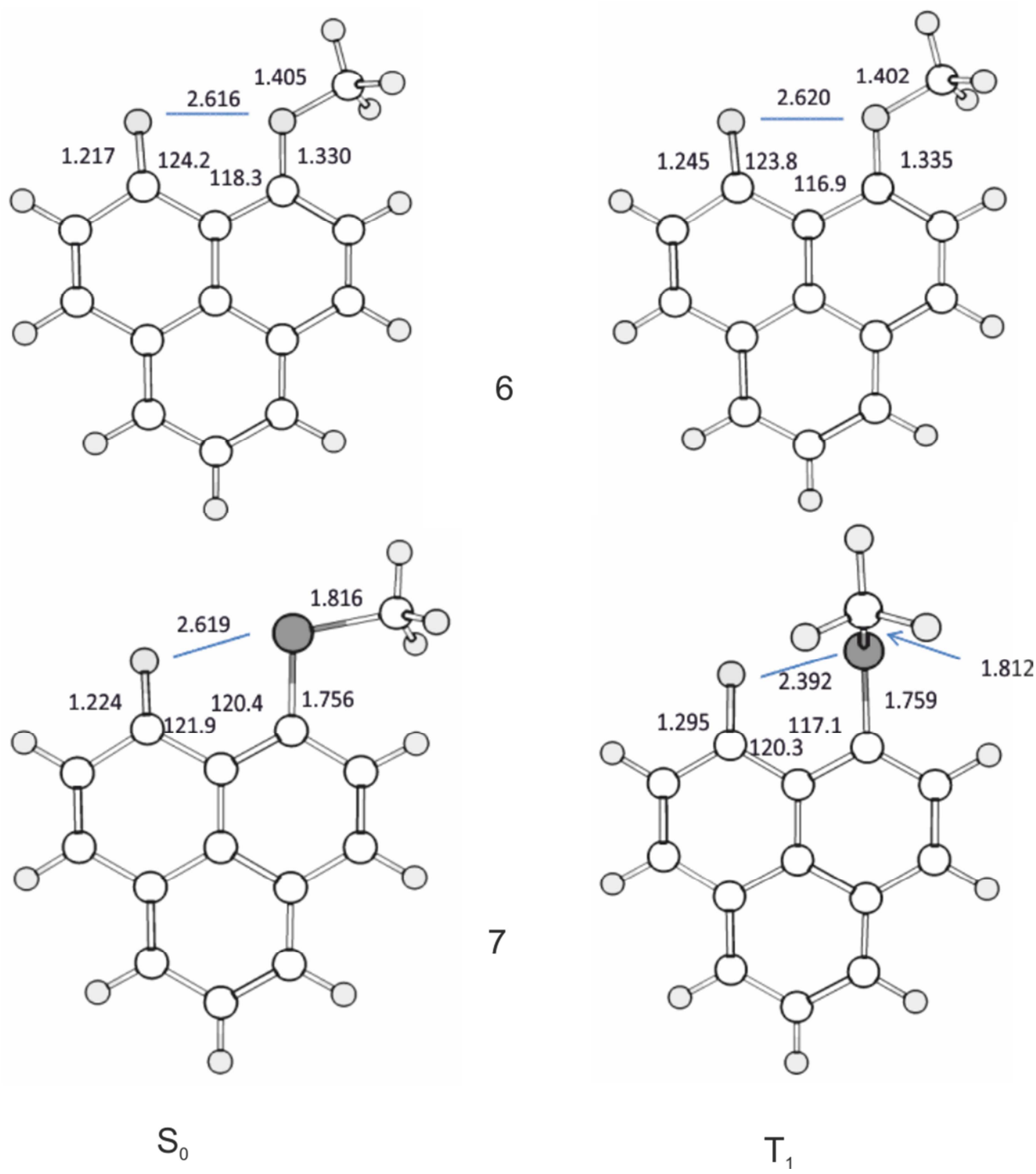


Figure 4: Optimized geometries (M06/cc-pVTZ, gas phase) of 9-methoxyphenalenone **6** (top) and 9-methylthiophenalenone **7** (bottom). Left: singlet ground state. Right: Lowest triplet excited state.

9-Dimethylaminophenalenone (X = Me_2N): This compound differs from the systems dealt with so far in that the ground state singlet ketone no longer has a plane of symmetry. In case of the dimethylamino derivative **8**, the phenalenone system is predicted to be significantly twisted (M06/cc-pVTZ: D(NC_9C_1O) = 26.2˚), to minimise repulsion between carbonyl and methyl groups, while allowing for overlap of the nitrogen lone pair with the π-system. Pyramidalization at the nitrogen atom is calculated to be small (M06/cc-pVTZ: D($C_{(H3)}C_{(H3)}C_9N$) = 8.5˚), which is similar to other dimethyl aryl amines.[32]

9-Dimethylaminophenalenone **8** has a lowest triplet excited state of (σ*,π*) type, as indicated by a significant shortening of the N-O distance upon triplet excitation, and as also evidenced by the singly-occupied molecular orbitals.

Figure 5 shows calculated geometries (M06/cc-pVTZ) of the singlet ground state and first triplet excited state of **8**, Figure 6 displays the singly-occupied natural orbitals of the first triplet excited state of the same compound.

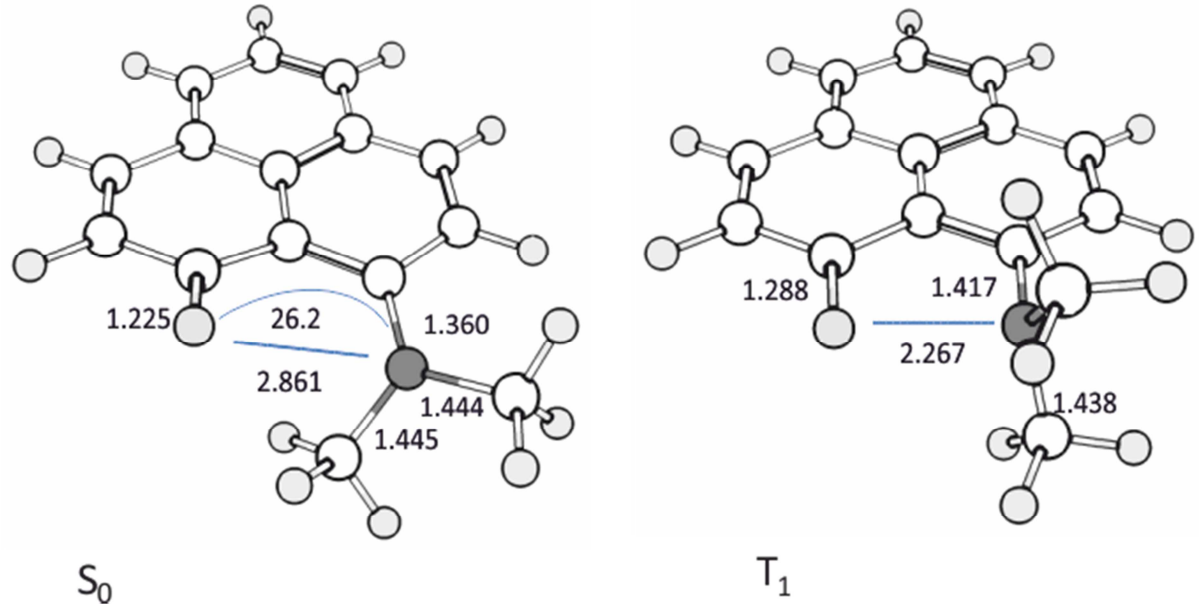


Figure 5: Optimized geometries (M06/cc-pVTZ, gas phase) of 9-dimethylaminophenalenone **8**. Left: singlet ground state. Right: first triplet excited state.

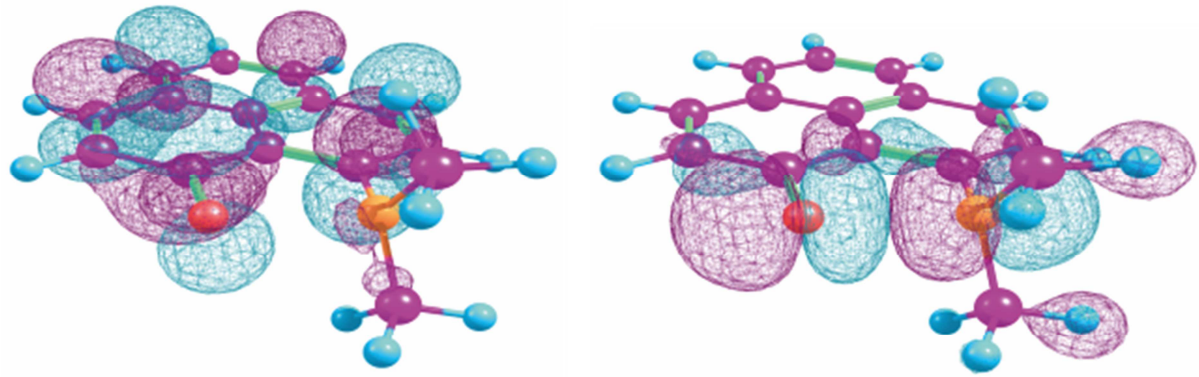


Figure 6: singly-occupied natural molecular orbitals (M05-2X/SDD, gas phase) for triplet 9-dimethylaminophenalenone **8**. Left: HOMO-1. Right: HOMO.

Figures 5 and 6 clearly show that the lowest triplet excited state of **8** is weakly bonding with respect to the N-O distance, which is due to an electron being taken out of a doubly-occupied N-O σ* orbital. Unlike in **4**, **5**, and **7**, the singly-occupied π* orbital in this (σ*,π*) triplet excited state is predicted to be energetically below the σ* orbital.

Electronic properties of phenalenones: spin and charge distribution. Electronic parameters such as charge and spin distribution, triplet energy, and energy difference between first and second excited triplet state provide insight into the nature of the triplet excited states investigated. Table 2 lists these parameters, for S_0 and T_1 of **1**-**8**.

Table 2: Selected electronic properties (electronic triplet energy, Mulliken spin density at the carbonyl oxygen atom, Mulliken spin density at atom X, APT charge at the carbonyl oxygen atom, APT charge at atom X, vertical energy difference between T_1 and T_2 at the geometry of T_1) of phenalenone derivatives **1**-**8**. Normal font: singlet ground state. In *italics*: first triplet excited state.

	X	Method	Type of T	E_T[kcal / mol]	Spin @O	Spin @X	Charge @O	Charge @X	$\Delta E_{T1,2(v)}$ [eV][a]
1	H	M05-2X/SDD	(π,π*)	42.5	*0.669*	*-0.011*	-0.812 *0.074*	0.095 *0.097*	*-0.404*
1	H	M06/SDD	(π,π*)	39.9	*0.560*	*-0.015*	-0.774 *-0.191*	0.082 *0.084*	*-0.635*
1	H	M06/SDD (DMF)	(π,π*)	40.9	*0.493*	*-0.015*	-1.220 *-0.411*	0.088 *0.089*	*-0.651*
1	H	M06/cc-pVTZ	(π,π*)	43.1	*0.402*	*-0.004*	-0.804 *-0.377*	0.070 *0.070*	*-0.728*
2	F	M05-2X/SDD	(π,π*)	43.5	*0.716*	*0.012*	-0.748 *0.118*	-0.486 *-0.506*	*-0.424*
2	F	M06/SDD	(π,π*)	41.0	*0.587*	*0.015*	-0.716 *-0.151*	-0.487 *-0.508*	*-0.192*
2	F	M06/SDD (DMF)	(π,π*)	41.8	*0.508*	*0.011*	-1.175 *-0.390*	-0.692 *-0.722*	*-0.514*
2	F	M06/cc-pVTZ	(π,π*)	44.9	*0.411*	*0.019*	-0.772 *-0.359*	-0.521 *-0.547*	*-0.592*
3	Cl	M05-2X/SDD	(π,π*)	43.4	*0.699*	*0.013*	-0.723 *0.086*	-0.266 *-0.280*	*-0.417*
3	Cl	M06/SDD	(π,π*)	40.8	*0.578*	*0.014*	-0.684 *-0.166*	-0.309 *-0.322*	*-0.145*
3	Cl	M06/SDD (DMF)	(π,π*)	41.3	*0.506*	*0.008*	-1.132 *-0.395*	-0.477 *-0.491*	*-0.448*
3	Cl	M06/cc-pVTZ	(π,π*)	44.3	*0.407*	*0.026*	-0.729 *-0.360*	-0.321 *-0.338*	*-0.517*
4	Br	M05-2X/SDD	(σ*,π*)	42.4	*0.961*	*0.097*	-0.716 *-0.346*	-0.186 *-0.278*	*0.388*
4	Br	M06/SDD	(σ*,π*)	41.0	*0.899*	*0.180*	-0.678 *-0.326*	-0.228 *-0.282*	*0.261*
4	Br	M06/SDD (DMF)	(π,π*)	41.5	*0.501*	*0.010*	-1.117 *-0.412*	-0.378 *-0.372*	*-0.424*
4	Br	M06/cc-pVTZ	(σ*,π*)	47.7	*0.842*	*0.204*	-0.718 *-0.326*	-0.209 *-0.253*	*0.314*
5	I	M05-2X/SDD	(σ*,π*)	41.5	*0.832*	*0.253*	-0.714 *-0.284*	-0.070 *-0.311*	*0.379*
5	I	M06/SDD	(σ*,π*)	39.2	*0.787*	*0.309*	-0.673 *-0.370*	-0.108 *-0.167*	*0.401*

5	I	M06/SDD (DMF)	(σ*,π*)	42.2	*0.733*	*0.359*	-1.117 *-0.563*	-0.189 *-0.253*	*0.444*
6	MeO	M05-2X/SDD	(π,π*)	43.6	*0.724*	*0.053*	-0.735 *0.091*	-0.889 *-0.966*	*-0.392*
6	MeO	M06/SDD	(π,π*)	41.2	*0.595*	*0.054*	-0.701 *-0.126*	-0.883 *-0.930*	*-0.114*
6	MeO	M06/SDD (DMF)	(π,π*)	43.3	*0.516*	*0.048*	-1.150 *-0.374*	-1.190 *-1.291*	*-0.397*
6	MeO	M06/cc-pVTZ	(π,π*)	44.6	*0.412*	*0.049*	-0.756 *-0.355*	-0.940 *-0.999*	*-0.546*
7	MeS	M05-2X/SDD	(σ*,π*)	37.9	*0.653*	*0.459*	-0.740 *-0.586*	-0.098 *0.029*	*0.978*
7	MeS	M06/SDD	(σ*,π*)	38.1	*0.729*	*0.346*	-0.716 *-0.473*	-0.079 *-0.032*	*0.768*
7	MeS	M06/SDD (DMF)	(σ*,π*)	41.8	*0.670*	*0.401*	-1.139 *-0.734*	-0.208 *-0.020*	*0.829*
7	MeS	M06/cc-pVTZ	(σ*,π*)	43.7	*0.591*	*0.488*	-0.735 *-0.577*	-0.078 *0.165*	*1.098*
8	Me_2N	M05-2X/SDD	(σ*,π*)	39.2	*0.640*	*0.468*	-0.742 *-0.778*	-0.869 *-0.184*	*1.519*
8	Me_2N	M06/SDD	(σ*,π*)	39.2	*0.646*	*0.428*	-0.703 *-0.727*	-0.813 *-0.148*	*1.119*
8	Me_2N	M06/SDD (DMF)	(σ*,π*)	40.2	*0.510*	*0.561*	-1.078 *-1.269*	-1.090 *0.205*	*1.285*
8	Me_2N	M06/cc-pVTZ	(σ*,π*)	44.8	*0.605*	*0.418*	-0.741 *-0.743*	-0.802 *-0.055*	*1.042*

[a]A negative value indicates a (π,π*) lowest triplet excited state, a positive value a (σ*,π*) lowest triplet excited state. Vertical excitation energies from TD-DFT.

A number of trends can be derived from Table 2. First, for the systems with lowest (σ*,π*) triplet states, the energy difference between first and second (π,π*) triplet excited states correlates with nucleophilicity of the substituent X – the more nucleophilic X, the more the (σ*,π*) state is favored over the (π,π*) state. In case of the systems with lowest (π,π*) state, an increase of nucleophilicity of X results in a decrease of the T_1-T_2 splitting. Second, for the systems with lowest (σ*,π*) triplet states, the triplet energy appears to correlate with the spin density present on the carbonyl oxygen – it is particularly high in case of **4**, where the Mulliken spin density at the carbonyl oxygen atom is particularly high, and lower for **7** or **8**, where the nitrogen or sulfur atoms accept significant spin density. Third, significant charge transfer is observed for dimethylamino-derivative **8**, where the nitrogen atom gives up approximately one full charge unit upon triplet excitation, but very little in the other derivatives investigated. Based on this pronounced degree of charge transfer, and on the significant change in geometry, the (σ*,π*) triplet excited state of **8** might be described as a twisted internal charge transfer (TICT) state.[33] 9-Bromophenalenone **4**, finally, is predicted to have a (σ*,π*) type lowest triplet excited in the gas phase, whereas it is calculated to be a (π,π*) triplet excited state in DMF solution (see Tables 1 and 2). This is likely due to the fact that the interaction of the oxygen lone pairs is only weak in the case of X = Br, making the system more prone to perturbation by other influences such as solvent polarity.

It appears unlikely that the state switching observed for triplet states of 9-substituted phenalenones should be limited to this particular system. In fact, the lowest triplet excited states of compounds such as 2-iodobenzophenone **9**, or 4-iodo-2-butanone **10** are also predicted to have lowest triplet excited states of ($\sigma*$,$\pi*$) character, indicating that state switching (or intramolecular triplet exciplex formation) can be assumed to be a general phenomenon in ketone photochemistry. However, the ring formed in intramolecular exciplex formation at least needs to be a five-membered ring – the lowest triplet excited state of iodoacetone **11**, where an intramolecular ($\sigma*$,$\pi*$) type exciplex would contain an O-C-C-I four-membered ring is calculated to undergo C-I cleavage. Figure 7 shows the lowest triplet excited states of **9**-**11**, optimized at the M06/SDD level of theory.

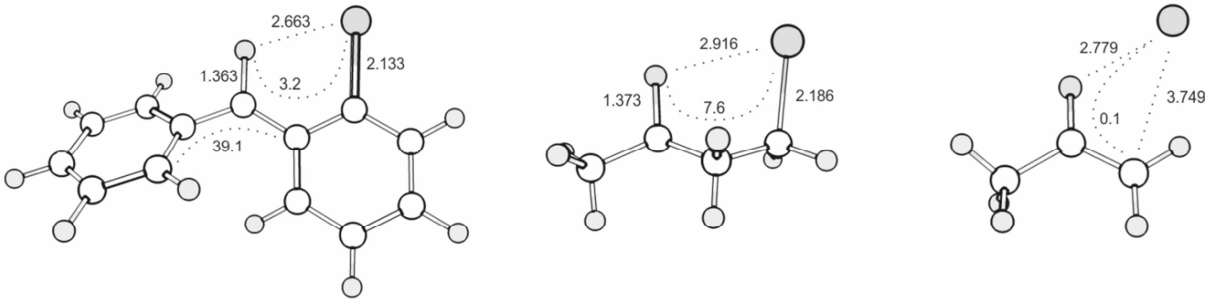


Figure 7: Optimized structures (M06/SDD) of the lowest triplet excited states of 2-iodobenzophenone **9** (left), 4-iodo-2-butanone **10** (middle), and iodoacetone **11** (right). Distances are given in Å, dihedral angles in °.

The geometries of the lowest triplet excited states of **9** bears similarity with triplet **5**, with very similar carbon-iodine and oxygen-iodine bond lengths. In case of the triplet state of **10**, the oxygen-iodine interaction is considerably weaker than in **5** or **9**, as evidenced by the much longer O-I distance. Nevertheless, the frontier orbitals clearly make this a ($\sigma*$,$\pi*$) type triplet state. In comparison, exciting **11** to its lowest triplet excited state results in carbon-iodine bond cleavage, while significant interaction remains between the iodine atom and carbonyl oxygen atom.

Conclusion

A systematic study on triplet excited states of 9-substituted derivatives of phenalenone shows that interaction between neighboring nucleophilic substituents (X = Br, I, SMe, NMe_2, but not F, Cl, OMe) and the carbonyl oxygen atom results in intramolecular exciplex formation, resulting in a switch from a (π,$\pi*$) type lowest triplet excited state to a ($\sigma*$,$\pi*$) type triplet excited state, which should bear similarity to a (n,$\pi*$) triplet excited state, with the added feature of significant spin density being present at the nucleophilic substituent. Preliminary calculations on other systems, such as 2-iodobenzophenone **9**, 4-iodo-2-butanone **10**, or iodoacetone **11** indicate that intramolecular ($\sigma*$,$\pi*$) type triplet exciplex formation likely is a more general phenomenon, as long as the ring being formed in exciplex formation at least is a five-membered ring. Intramolecular exciplex formation of a ketone excited state is consistent with the well-known formation of intermolecular triplet exciplexes.[9-11,34,35] In particular if X is a heavy halogen, it will dramatically increase the intersystem crossing rate constant via spin-orbit coupling, and therefore result in dramatically shortened excited state lifetimes.[36] An important new aspect is that the proximity between the substituent X and the carbonyl oxygen atom does not necessarily have to result in efficient C-X cleavage.[37] The photochemistry of 2-bromoacetophenone and 2-bromobenzophenone had previously been

investigated using ns LFP and product studies,[38] and the authors of this work had already stated that the very high reactivity of the triplet state of 2-bromobenzophenone "could reflect a direct, through-space charge transfer interaction between the bromine atom and the carbonyl…". According to the results presented here, the through-space interaction bears very little if any charge transfer character (with the exception of X = NR_2, where charge transfer is significant), but should nevertheless provide a deactivation pathway, via enhanced spin orbit coupling. This triplet deactivation mechanism might potentially be of relevance to applied fields of chemistry such as sunscreen formulations, in particular if nucleophilic substituents (like X = SR) are employed that are bound more strongly to the ketone framework.[39]

References

[1] N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Sausalito, CA, 1991.

[2] J. K. Bell, H. Linschitz, *J. Am. Chem. Soc.* **1963**, 85, 528-52. **doi**: 10.1021/ja00888a009.

[3] H. Lutz, M.-C. Duval, E. Bréhéret, L. Lindqvist, *J. Phys. Chem.* **1972**, 76, 821-2. **doi:** 10.1021/j100650a004.

[4] M. N. R. Ashfold, G. A. King, D. Murdock, M. G. D. Nix, T. A. A. Oliver, A. G. Sage, *PhysChemChemPhys* **2010**, 12, 1218-1238. **doi**: 10.1039/B921706A

[5] G. Bucher, C. Lu, W. Sander, *ChemPhysChem* **2005**, 6, 2607-2618. **doi**: 10.1002/cphc.200500211

[6] S. Ginagunta, G. Bucher, *J. Phys. Chem. A* **2011**, 115, 540-546. **doi:** 10.1021/jp108021k

[7] D. Zhang, *Monatsh. Chem*. **2010**, 141, 1279-1285. **doi**: 10.1007/s00706-010-0401-6

[8] J. G. Hill, G. Bucher, *J. Phys. Chem. A* **2014**, 118, 2332-2343. **doi:** 10.1021/jp500766d

[9] D. Klapstein, U. Pischel, W. M. Nau, *J. Am. Chem. Soc.* **2002**, 124, 11349-57. **doi:** 10.1021/ja020400h

[10] S.-C. Chen, T.-S. Fang, *Chem. Phys. Lett*. **2007**, 450, 65-70. **doi**: 10.1016/j.cplett.2007.11.011

[11] U. Pischel, W. M. Nau, *J. Am. Chem. Soc.* **2001**, 123, 9727-37. **doi**: 10.1021/ja011212e

[12] E. Oliveros, P. Suardi-Murasecco, T. Aminian-Saghafi, A. M. Braun, *Helv. Chim. Acta* **1991**, 74, 79-90. **doi**: 10.1002/hlca.19910740110

[13] M. C. Daza, M. Doerr, S. Salzmann, C. M. Marian, W. Thiel, *Phys. Chem. Chem. Phys.* **2009**, 11, 1688-96. **doi**: 10.1039/B815724C

[14] C. Flors, P. R. Ogilby, J. G. Luis, T. A. Grillo, L. R. Izquierdo, P.-L. Gentilli, L. Bussoti, S. Nonell, *Photochem. Photobiol.* **2006**, 82, 95-103. **doi**: 10.1562/2005-04-07-RA-479

[15] O. Anamimoghadam, M. D. Symes, C. Busche, D. Long, S. T. Caldwell, C. Flors, S. Nonell, L. Cronin, G. Bucher, *Org. Lett*. **2013**, 15, 2970-2973. **doi**: 10.1021/ol401117g

[16] G. Bucher, R. Bresolí-Obach, C. Brosa, C. Flors, J. G. Luis, T. A. Grillo, S. Nonell, *PhysChemChemPhys* **2014**, 16, 18813-20. **doi**: 10.1039/C4CP02783C

[17] O. Anamimoghadam, M. Symes, S. Sproules, D. Long, L. Cronin, G. Bucher, *J. Am. Chem. Soc.* **2015**, 137, 14944-51. **doi**: 10.1021/jacs.5b07959

[18] O. Anamimoghadam, D. Long, G. Bucher, *RSC Advances* **2014**, 4, 56654-7. **doi**: 10.1039/C4RA00178H

[19] Gaussian 09, Revision **A.02**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S.

Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[20] Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory and Comput.* **2006**, 2, 364-82. **doi**: 10.1021/ct0502763
[21] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, 120, 215-41. **doi**: 10.1007/s00214-007-0310-x
[22] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, 105, 2999-3093. **doi**: 10.1021/cr9904009
[23] S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, 55, 117-29. **doi**: 10.1016/0301-0104(81)85090-2
[24] T. H. Dunning Jr., P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York), **1977**, 1-28.
[25] G. Igel-Mann, H. Stoll, H. Preuss, *Mol. Phys.* **1988**, 65, 1321-28. **doi**: 10.1080/00268978800101811
[26] T. H. Dunning Jr., *J. Chem. Phys.* **1989**, 90, 1007-23. **doi**: 10.1063/1.456153
[27] R. A. Kendall, T. H. Dunning Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, 96, 6796-806. **doi**: 10.1063/1.462569
[28] D. E. Woon, T. H. Dunning Jr., *J. Chem. Phys.* **1993**, 98, 1358-71. **doi**: 10.1063/1.464303
[29] G. C. Pimentel, *J. Chem. Phys.* **1951**, 19, 446-8. **doi**: 10.1063/1.1748245
[30] E. Magnusson, *J. Am. Chem. Soc.* **1990**, 112, 7940-51. **doi**: 10.1021/ja00178a014
[31] For the relevant orbitals, please see the Supporting Information.
[32] V. P. Novikov, S. Samdal, L. V. Vilkov, *Russ. J. Gen. Chem.* **2004**, 74, 1247-53. **doi**:10.1007/s11176-005-0146-9
[33] S. Sasaki, G. P. C. Drummen, G. Konishi, *J. Mat. Chem. C*. **2016**, 4, 2731-43. **doi**: 10.1039/c5tc03933a
[34] P. Jacques, X. Allonas, M. Von Raumer, P. Suppan, E. Haselbach, *J. Photochem. Photobiol. A: Chem.* **1997**, 111, 41-45. **doi**: 10.1016/S1010-6030(97)00238-4
[35] C. Devadoss, R. W. Fessenden*, J. Phys. Chem.* **1990**, 94, 4540-9. **doi**: 10.1021/j100374a036
[36] Preliminary ns time-resolved laser flash photolysis experiments with **5** (355 nm excitation wavelength, 8 ns pulse duration, 80 mJ / pulse, CH_3CN, 1 atm. Ar) did not show any transient species decaying on the ns or longer timescales. While this negative evidence is not conclusive, it would be consistent with the T_1 lifetime of **5** being very short. It may also point to C-I cleavage being inefficient, as the phenyl-type radical and / or an iodine atom complex would have had to be observed otherwise. O. Anamimoghadam, G. Bucher, unpublished work.
[37] The observation that the C-I bond length does not vary between S_0 and T_1 of **5** would support this. However, upon extremely rapid radiationless deactivation of the excited state, cleavage of the relatively weak C-I bond in a hot ground state ketone might nevertheless occur.
[38] P. J. Wagner, J. H. Sedon, A. Gudmundsdottir, *J. Am. Chem. Soc.* **1996**, 118, 746-54. **doi**: 10.1021/ja952782f
[39] Excited states of *o*-thiyl ketones have been reported to be deactivated efficiently via a charge transfer interaction, see ref. [38] and Q. Cao, PhD Thesis, Michigan State University, 1990.